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(71) Applicant: UBE INDUSTRIES, LTD.
Ube-shi, Yamaguchi-ken 755 (JP)

(72) Inventors:
- Fukuda, Koichi
Ube-shi, Yamaguchi (JP)
- Fujinaga, Masataka
Ube-shi, Yamaguchi (JP)
- Mitani, Atsuyuki
Ube-shi, Yamaguchi (JP)
- Takeda, Masatoshi
Ube-shi, Yamaguchi (JP)
- Ishitobi, Shinichi
Ube-shi, Yamaguchi (JP)

(74) Representative: Zumstein, Fritz, Dr. et al
Zumstein & Klingseisen
Patentanwälte
Bräuhausstrasse 4
D-80331 München (DE)

(54) Dielectric ceramic composition

(57) A dielectric ceramic composition mainly comprises a major component which comprises barium, titanium, neodymium, samarium and oxygen and is represented by the following compositional formula:

$xBaO\text{-}yTiO_2\text{-}zNd_2O_3\text{-}tSm_2O_3$

(wherein $0.1 \leq x \leq 0.2$; $0.5 \leq y \leq 0.8$; $0.01 \leq z \leq 0.2$; $0 \leq t \leq 0.2$, provided that $x+y+z+t = 1$); and a minor component mainly comprising glass powder having a softening point of about 100 to about 500°C, which mainly comprises PbO, ZnO and B_2O_3, and GeO_2, and wherein the content (a) (% by weight) of the glass powder falls within the range of $1 \leq a \leq 25$ and the content (b) (% by weight) of GeO_2 falls within the range of $0.5 \leq b \leq 10$, on the basis of the weight of the major component. The major component may further comprise Bi_2O_3 and the composition may comprise bismuth as a minor component. The dielectric ceramic composition can be sintered at a low temperature and exhibits excellent characteristic properties such that it has a large specific dielectric constant ε_r, a large unloaded Q and a small temperature coefficient of the resonance frequency.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a dielectric ceramic composition suitably used as a material for a dielectric resonator or the like.

Disclosure of the Prior Art:

There has recently been desired for the development of a small-sized and high performance dielectric resonator as integration of microwave circuits is increased. The dielectric ceramic composition used in such dielectric resonators must satisfy various requirements. For instance, the composition should have a large specific dielectric constant ε_r, a large unloaded Q and a low temperature coefficient of resonance frequency τ_f.

As examples of such dielectric ceramic compositions, Ber. Dt. Keram. Ges., 55 (1978), Nr. 7 and JPA No. Sho 60-35406 propose dielectric ceramic compositions comprising BaO-TiO_2-Nd_2O_3 systems. Moreover, U.S. Patent No. 5,292,694 discloses a dielectric ceramic composition comprising a BaO-TiO_2-RE_2O_3 system (wherein "RE" represents a rare earth metal). In addition, JPA No. Sho 62-72558 discloses a dielectric ceramic composition comprising a BaO-TiO_2-Nd_2O_3-Bi_2O_3 system.

There have recently been developed a laminated chip condenser and a laminated dielectric resonator, which are prepared by laminating a dielectric ceramic composition. In this respect, the ceramic composition and the internal electrode have been laminated by simultaneous firing. However, it is difficult to simultaneously firing the foregoing dielectric ceramic composition and the internal electrode, since the firing temperature of the former is high on the order of 1300 to 1400 °C and therefore, electrode materials for producing laminated structures are limited to those which are proof against a high temperature such as palladium (Pd) and platinum (Pt). For this reason, there has long been desired for the development of a dielectric ceramic composition capable of being fired simultaneously with cheaper electrode materials such as silver (Ag), silver-palladium (Ag-Pd) and copper (Cu), at a low temperature of not higher than 1200°C.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a dielectric ceramic composition which has excellent properties as a material for dielectric resonators or the like, in particular, a high dielectric constant, a high unloaded Q and low temperature-dependency of the resonance frequency and which exhibits good sinterability even if it is fired at a low temperature.

According to an aspect of the present invention, there is provided a dielectric ceramic composition which mainly comprises a major component comprising barium, titanium, neodymium, samarium and oxygen and represented by the following compositional formula:

$$xBaO\text{-}yTiO_2\text{-}zNd_2O_3\text{-}tSm_2O_3 \qquad (1)$$

(wherein $0.1 \leqq x \leqq 0.2$; $0.5 \leqq y \leqq 0.8$; $0.01 \leqq z \leqq 0.2$; $0 \leqq t \leqq 0.2$, provided that $x+y+z+t = 1$); and

a minor component mainly comprising glass powder, which mainly comprises PbO, ZnO and B_2O_3, and GeO_2, and wherein

the content (a) (% by weight) of the glass powder falls within the range of $1 \leqq a \leqq 25$ and the content (b) (% by weight) of GeO_2 falls within the range of $0.5 \leqq b \leqq 10$, on the basis of the weight of the major component.

According to another aspect of the present invention, there is provided a dielectric ceramic composition mainly comprising a major component which comprises barium, titanium, neodymium, samarium, bismuth and oxygen and is represented by the following compositional formula:

$$xBaO\text{-}yTiO_2\text{-}zNd_2O_3\text{-}tSm_2O_3\text{-}wBi_2O_3 \qquad (2)$$

(wherein $0.1 \leqq x \leqq 0.2$; $0.5 \leqq y \leqq 0.8$; $0.01 \leqq z \leqq 0.2$; $0.01 \leqq t \leqq 0.2$; $0.005 \leqq w \leqq 0.05$, provided that $x+y+z+t+w = 1$); and

a minor component mainly comprising glass powder, which mainly comprises PbO, ZnO and B_2O_3, and GeO_2, and wherein

the content (a) (% by weight) of the glass powder falls within the range of $1 \leqq a \leqq 25$ and the content (b) (% by weight) of GeO_2 falls within the range of $0.5 \leqq b \leqq 10$, on the basis of the weight of the major component.

The dielectric ceramic composition of the present invention may further comprise Li_2O as a minor component and the content (c) (% by weights of Li_2O falls within the range of $0.04 \leqq c \leqq 4$ on the basis of the weight of the major component.

The dielectric ceramic composition may also contain Nb_2O_5, MnO, Al_2O_3 and/or ZnO.

In the ceramic composition of this invention, the content of PbO, ZnO and B_2O_3 in the glass powder are preferably in the range of $5 \leq PbO \leq 90$ $5 \leq B_2O_3 \leq 60$ and $0 < ZnO \leq 65$, more preferably $0 < ZnO \leq 50$ (% by weight).

If the softening point of the glass powder is higher than about 500°C, it becomes difficult to fire at a low temperature. Although there is no limitation on the lower limit of the softening point of the glass powder, it is usually about 100°C.

It has been found that the dielectric ceramic composition of this invention has excellent characteristic properties such that it can be sintered at a low temperature and that it has a high dielectric constant, a large unloaded Q and low temperature-dependency of the resonance frequency.

The present invention is also provides a dielectric device such as a dielectric resonator and a dielectric filter, comprising the dielectric ceramic composition as above.

DETAILED DESCRIPTION OF THE INVENTION

First, the relative amounts of the oxides constituting the major component of the dielectric ceramic composition according to the present invention will be explained below. If the molar fraction of BaO exceeds the foregoing upper limit, the dielectric resonator produced from the resulting dielectric ceramic composition does not undergo any resonance. On the other hand, if it is less than the lower limit, the resulting dielectric resonator exhibits a low dielectric constant and a low unloaded Q.

If the molar fraction of TiO_2 is greater than the upper limit defined above, the resulting dielectric resonator shows a large temperature coefficient of the resonance frequency, while if it is less than the lower limit, the dielectric constant of the resulting resonator is low. Moreover, if the molar fraction of Nd_2O_3 is greater than the upper limit defined above, the resulting dielectric resonator exhibits a low dielectric constant and a low unloaded Q, while if it is less than the lower limit, the temperature coefficient of the resonance frequency observed for the resulting dielectric resonator has a tendency to increase. In addition, the molar fraction of Sm_2O_3 has an effect on the dielectric constant, the unloaded Q and the temperature coefficient of the resonance frequency of the resulting dielectric resonator and therefore, a dielectric resonator exhibiting the desired characteristic properties can be produced only when it falls within the range defined above.

In the present invention, if the content of the minor component relative to the major component, i.e., the content (a) (% by weight) of the glass powder which mainly comprises PbO, ZnO and B_2O_3 and the content (b) (% by weight) of GeO_2 are extremely high, the unloaded Q of the resulting dielectric resonator is reduced, while these contents (a) and (b) are too low or zero, it becomes difficult to fire the resulting composition at a low temperature of not higher than 1200 °C. For this reason, the content of the minor component relative to the major component, i.e., the content (a) (% by weight) of the glass powder which mainly comprises PbO, ZnO and B_2O_3 and the content (b) (% by weight) of GeO_2 are limited to the foregoing ranges, respectively. Moreover, the relative proportions of PbO, ZnO and B_2O_3 which constitute the glass powder are not particularly restricted, but if the content of ZnO is too high, the softening point of the resulting glass increases and it is difficult to fire the resulting composition at a low temperature. Accordingly, the content of ZnO in the glass powder is preferably $0 < ZnO \leq 65$, more preferably $0 < ZnO \leq 50$. The content of PbO and B_2O_3 falls preferably within $5 \leq PbO \leq 90$ and $5 \leq B_2O_3 \leq 60$ (% by weight), respectively.

And, if the softening point of the minor comonent, glass powder, is higher than about 500°C, it becomes difficult to fire at a low temperature.

The dielectric ceramic composition of the present invention may further comprise, as a minor component, Li_2O such that the content (c) (% by weight) thereof falls within the range of $0.04 \leq c \leq 4$. The addition of Li_2O permits a further decrease of the sintering temperature of the composition and as a result, an internal electrode of Ag can easily be formed. If the content (c) of Li_2O exceeds the upper limit defined above, the dielectric resonator produced from the resulting dielectric ceramic composition never undergoes resonance.

According to a second aspect of the present invention, there is further provided a dielectric ceramic composition which mainly comprises a major component comprising barium, titanium, neodymium, samarium, bismuth and oxygen and represented by the following compositional formula:

$$xBaO\text{-}yTiO_2\text{-}zNd_2O_3\text{-}tSm_2O_3\text{-}wBi_2O_3 \qquad (2)$$

(wherein $0.1 \leq x \leq 0.2$; $0.5 \leq y \leq 0.8$; $0.01 \leq z \leq 0.2$; $0.01 \leq t \leq 0.2$; $0.005 \leq w \leq 0.05$, provided that $x+y+z+t+w = 1$); and

a minor component mainly comprising glass powder, which mainly comprises PbO, ZnO and B_2O_3, and GeO_2, and wherein

the content (a) (% by weight) of the glass powder falls within the range of $1 \leq a \leq 25$ and the content (b) (% by weight) of GeO_2 falls within the range of $0.5 \leq b \leq 10$, on the basis of the weight of the major component.

If the softening point of the minor comonent, glass powder is higher than about 500°C, it becomes difficult to fire at a low temperature.

In this composition, if the molar fraction of Bi_2O_3 is excessively high, the resulting composition exhibits a low dielectric constant and a low unloaded Q, while if it is extremely low, the dielectric resonator produced from the resulting composition has a high temperature coefficient of the resonance frequency. In the foregoing formula (2), the proportions of x, y, z and t as well as the contents (a) and (b) of the glass powder and GeO_2 as the minor component are limited to the foregoing ranges respectively, for the same reasons discussed above in connection with the foregoing formula (1).

This dielectric ceramic composition has excellent characteristic properties like the foregoing composition according to the first aspect such that it can also be sintered at a low temperature and that it has a high dielectric constant, a large unloaded Q and low temperature-dependency of the resonance frequency.

The dielectric ceramic composition according to the second aspect of the present invention may further comprise, as a minor component, Li_2O such that the content (c) (% by weight) thereof falls within the range of $0.04 \leq c \leq 4$. In this case, the addition of Li_2O likewise permits a further decrease of the sintering temperature of the composition and as a result, an internal electrode of Ag can easily be formed. If the content (c) of Li_2O exceeds the upper limit defined above, the dielectric resonator produced from the resulting dielectric ceramic composition never undergoes resonance.

In the present invention (the first and second aspects), at least one member selected from the group consisting of Nb_2O_5, MnO, Al_2O_3 and ZnO may be added to the composition as the third component and this permits a further reduction in the absolute value of the temperature coefficient τ_f of the resonance frequency. If the content d (% by weight) of the third component on the basis of the major component is extremely high, the temperature coefficient τ_f of the resonance frequency increases. Therefore, the content (d) thereof falls within the range of $0 \leq d \leq 2$, preferably $0.1 \leq d \leq 2$.

Then a preferred method for preparing the dielectric ceramic composition of the present invention will be described below.

A starting material comprising various oxides constituting the major component, for instance, barium carbonate, titanium oxide, neodymium oxide, samarium oxide and, if necessary, bismuth oxide is subjected to wet blending in predetermined portions together with a solvent such as water or an alcohol. Subsequently, the solvent such as the water or the alcohol was removed, followed by pulverization of the mixture and then calcination thereof at a temperature ranging from 1000 to 1300 °C for about 1 to 5 hours in an oxygen-containing gas atmosphere (for instance, in the air). The calcined powder thus prepared is wet-blended with the minor component, i.e., the glass powder which is composed of PbO, ZnO and B_2O_3 and GeO_2, and if necessary, Li_2O and the third component, i.e., at least one member selected from the group consisting of Nb_2O_5, MnO, Al_2O_3 and ZnO in the presence of a solvent such as an alcohol. Then the solvent such as the water or the alcohol is removed and thereafter the mixture is pulverized. Moreover, the product is uniformly mixed with an organic binder such as polyvinyl alcohol, followed by drying, pulverization and pressure molding (under a pressure ranging from about 100 to 1000 kg/cm^2). Thereafter, a dielectric ceramic composition represented by the foregoing compositional formula (1) or (2) can be obtained by firing the resulting molded article at a temperature ranging from 850 to 1100 °C in an oxygen-containing gas atmosphere, for instance, in the air.

The dielectric ceramic composition thus prepared may be, according to need, processed into appropriate shapes and sizes, or formed into a sheet by, for instance, the doctor blade technique followed by lamination of the sheet with an electrode and may thus be used as a material for a dielectric resonator, a dielectric substrate, a laminated element or the like.

As raw materials for barium, titanium, neodymium, samarium, niobium, bismuth, lead, zinc, boron, germanium, manganese, aluminum and lithium, there may be used, for instance, nitrates and hydroxides thereof which are converted into oxides during the firing process in addition to oxides thereof such as $BaCO_3$, TiO_2, Nd_2O_3, Sm_2O_3, Bi_2O_3, PbO, ZnO, B_2O_3, GeO_2, Nb_2O_5, MnO, Al_2O_3 and LiO_2

The present invention will hereinafter be described in more detail with reference to the following non-limitative working Examples and Comparative Examples.

Example 1

Barium carbonate powder ($BaCO_3$; 0.13 mole), titanium oxide powder (TiO_2; 0.70 mole) and neodymium oxide powder (Nd_2O_3; 0.17 mole) were charged in a ball mill together with ethanol and then subjected to wet blending for 12 hours. After the removal of the solvent from the dispersion, the mixture was pulverized and then calcined at 1250 °C in the air. Separately, glass powder A comprising 84wt% of lead oxide powder (PbO), 7 wt% of zinc oxide powder (ZnO) and 9 wt% of boron oxide powder (B_2O_3) was prepared according to the usual method. To the calcined product prepared above, there were added 2 wt% of the glass powder A comprising PbO, ZnO and B_2O_3, and 3 wt% of germanium oxide powder (GeO_2), followed by introduction of the mixture into a ball mill together with ethanol and then wet blending for 48 hours. After the removal of the solvent from the dispersion, the mixture was pulverized, followed by addition of an appropriate amount of a polyvinyl alcohol solution to the pulverized product, drying the mixture, forming it into pellets having a diameter of 12 mm and a thickness of 4 mm and then firing the pellets at 970°C for 2 hours in the air. The composition of the product and the sintering temperature thereof are summarized in the following Table 1.

The ceramic composition thus prepared was processed into pieces each having a diameter of 7 mm and a thickness of about 3 mm and inspected for the specific dielectric constant ε_r, the unloaded Q and the temperature coefficient τ_f of

the resonance frequency at a resonance frequency (ranging from 3 to 6 GHz) according to the dielectric resonance method. The results thus obtained are listed in the following Table 2.

Examples 2 to 22 and Comparative Examples 1 to 12

The same procedures used in Example 1 were repeated except that the mixing ratio of barium carbonate, titanium oxide, neodymium oxide and samarium oxide; the kinds of glass powder comprising PbO, ZnO and B_2O_3 (glass powder B: 80 wt% PbO, 10 wt% ZnO and 10 wt% B_2O_3) and the added amounts of the minor components as well as the added amount (d) of the third component were changed as detailed in Table 1 to prepare dielectric ceramic compositions and they were inspected for characteristic properties. The compositions of the products prepared in these Examples and

Comparative Examples and characteristic properties thereof are summarized in Table 2.

TABLE 1

	COMPOSITION OF DIELECTRIC CERAMIC								CALCINATION TEMPERATURE °C
	BaO x	TiO_2 y	Nd_2O_3 z	Sm_2O_3 t	GLASS POWDER wt%	KIND OF GLASS	GeO_2 wt%	d wt%	
EXAMPLE									
1	0.13	0.70	0.17	0	2	A	3	-	970
2	0.18	0.67	0.11	0.04	7	A	3	-	940
3	0.18	0.67	0.11	0.04	10	A	3	-	915
4	0.18	0.67	0.11	0.04	15	A	3	-	890
5	0.16	0.67	0.11	0.06	20	A	2	-	880
6	0.18	0.66	0.13	0.03	5	B	5	-	990
7	0.17	0.67	0.10	0.06	10	B	3	-	960
8	0.16	0.65	0.17	0.02	15	B	3	-	940
9	0.13	0.70	0.17	0	7	A	3	-	950
10	0.13	0.70	0.15	0.02	7	A	3	-	945
11	0.13	0.70	0.12	0.05	7	A	3	-	950
12	0.14	0.71	0.04	0.11	10	A	5	-	935
13	0.17	0.66	0.17	0	10	A	5	-	925
14	0.17	0.66	0.17	0	10	A	7	-	915
15	0.17	0.66	0.17	0	10	A	10	-	935
16	0.16	0.65	0.18	0.01	7	A	3	-	940
17	0.15	0.67	0.18	0	10	A	5	-	905
18	0.15	0.67	0.18	0	15	A	3	-	875
19	0.15	0.67	0.18	0	12	A	5	0.5(Nb_2O_5)	910
20	0.15	0.67	0.18	0	12	A	5	0.5(MnO)	915
21	0.15	0.67	0.18	0	12	A	5	0.5(Al_2O_3)	920
22	0.15	0.67	0.18	0	12	A	5	0.5(ZnO)	910
COMPARATIVE EXAMPLE									
1	0.05	0.75	0.19	0.01	10	A	5	-	960
2	0.30	0.57	0.11	0.02	10	A	3	-	935
3	0.08	0.86	0.05	0.01	15	A	3	-	920
4	0.15	0.45	0.39	0.01	9	A	2	-	930
5	0.11	0.57	0.31	0.01	10	A	2	-	920
6	0.10	0.89	0	0.01	10	A	2	-	925
7	0.14	0.55	0.01	0.30	5	A	3	-	945
8	0.15	0.70	0.13	0.02	0	-	0	-	1420
9	0.16	0.67	0.11	0.06	30	A	2	-	870
10	0.16	0.65	0.17	0.02	30	B	3	-	860
11	0.17	0.66	0.17	0	20	A	0	-	1160
12	0.15	0.70	0.13	0.02	10	A	15	-	890

TABLE 2

	ELECTRIC CHARACTERISTICS		
	ε_r	Q	τ_f ppm/°C
EXAMPLE			
1	71.0	1510	13
2	76.0	1190	6
3	70.0	1120	-5
4	68.0	910	-8
5	65.0	660	-22
6	74.0	1080	12
7	70.0	750	-7
8	67.0	615	-5
9	69.0	1305	8
10	69.5	1180	-7
11	68.0	975	21
12	61.0	715	-2
13	68.0	1060	18
14	64.0	1020	14
15	58.0	910	8
16	71.0	1120	16
17	62.0	1070	-46
18	66.0	720	-49
19	61.0	1100	-30
20	63.0	1120	-25
21	62.0	1090	-32
22	61.0	1110	-21
COMPARATIVE EXAMPLE			
1	44.0	150	-1
2	NO RESONANCE		
3	64.0	305	140
4	35.0	205	45
5	43.0	80	-6
6	60.0	1510	86
7	41.0	260	-31
8	87.0	2870	18
9	27.0	195	-7
10	23.0	145	7
11	94.0	80	81
12	41.0	220	-43

Example 23

Barium carbonate powder ($BaCO_3$; 0.13 mole), titanium oxide powder (TiO_2; 0.70 mole) and neodymium oxide powder (Nd_2O_3; 0.17 mole) were charged in a ball mill together with ethanol and then subjected to wet blending for 12 hours. After the removal of the solvent from the dispersion, the mixture was pulverized and then calcined at 1250 °C in the air. Separately, glass powder A comprising 84wt% of lead oxide powder (PbO), 7 wt% of zinc oxide powder (ZnO) and 9 wt% of boron oxide powder (B_2O_3) was prepared according to the usual method. To the calcined product prepared above, there were added 2 wt% of the glass powder A comprising PbO, ZnO and B_2O_3 as well as 3 wt% of germanium oxide powder (GeO_2) and 1 wt% (corresponding to 0.4 wt% as expressed in terms of the amount of Li_2O) of lithium carbonate powder (Li_2CO_3), followed by introduction of the mixture into a ball mill together with ethanol and then wet blending for 48 hours. After the removal of the solvent from the dispersion, the mixture was pulverized, followed by addition of an appropriate amount of a polyvinyl alcohol solution to the pulverized product, drying the mixture, forming it into pellets having a diameter of 12 mm and a thickness of 4 mm and then firing the pellets at 955°C for 2 hours in the air. The composition of the product and the sintering temperature thereof are summarized in the following Table 3.

The ceramic composition thus prepared was inspected for various characteristic properties which were determined under the same conditions used in Example 1. The results thus obtained are listed in the following Table 5.

Examples 24 to 47 and Comparative Examples 13 to 28

The same procedures used in Example 23 were repeated except that the mixing ratio of barium carbonate, titanium oxide, neodymium oxide and samarium oxide; the kinds of glass powder as a minor component mainly comprising PbO, ZnO and B_2O_3 in the ratio listed in Table 4 and the added amounts of the minor components were changed as detailed in Table 3 to prepare dielectric ceramic compositions and they were inspected for characteristic properties. The results

thus obtained are summarized in Table 5.

TABLE 3

	COMPOSITION OF DIELECTRIC CERAMIC								CALCINATION TEMPERATURE °C
	BaO x	TiO_2 y	Nd_2O_3 z	Sm_2O_3 t	GLASS POWDER wt%	KIND OF GLASS	GeO_2 wt%	Li_2O wt%	
EXAMPLE									
23	0.13	0.70	0.17	0	2	A	3	0.4	955
24	0.18	0.67	0.11	0.04	7	A	3	0.2	930
25	0.18	0.67	0.11	0.04	10	A	3	0.2	900
26	0.18	0.67	0.11	0.04	15	A	3	0.2	885
27	0.16	0.67	0.11	0.06	20	A	2	0.4	855
28	0.18	0.66	0.13	0.03	5	B	5	0.4	970
29	0.17	0.67	0.10	0.06	10	B	3	0.8	940
30	0.16	0.65	0.17	0.02	15	B	3	0.4	910
31	0.13	0.70	0.17	0	7	A	3	0.4	930
32	0.13	0.70	0.15	0.02	7	A	3	0.4	925
33	0.13	0.70	0.12	0.05	7	A	3	0.4	925
34	0.14	0.71	0.04	0.11	10	A	5	0.2	930
35	0.17	0.66	0.17	0	10	A	5	0.2	915
36	0.17	0.66	0.17	0	10	A	7	0.2	910
37	0.17	0.66	0.17	0	10	A	10	0.2	930
38	0.16	0.65	0.18	0.01	7	A	3	0.2	935
39	0.16	0.65	0.18	0.01	7	A	3	0.4	915
40	0.16	0.65	0.18	0.01	7	A	3	0.6	905
41	0.16	0.65	0.18	0.01	7	A	3	0.8	885
42	0.15	0.67	0.18	0	10	A	5	0.4	880
43	0.15	0.67	0.18	0	15	A	3	0.4	850
44	0.17	0.66	0.17	0	20	C	-	-	950
45	0.16	0.67	0.17	0	18	D	-	-	940
46	0.16	0.67	0.17	0	20	E	-	-	940
47	0.16	0.66	0.18	0	17	F	5	0.3	850
COMPARATIVE EXAMPLE									
13	0.05	0.75	0.19	0.01	10	A	5	0.2	945
14	0.30	0.57	0.11	0.02	10	A	3	0.2	930
15	0.08	0.86	0.05	0.01	15	A	3	0.4	890
16	0.15	0.45	0.39	0.01	9	A	2	0.6	900
17	0.11	0.57	0.31	0.01	10	A	2	0.8	890
18	0.10	0.89	0	0.01	10	A	2	0.4	910
19	0.14	0.55	0.01	0.30	5	A	3	0.4	920
20	0.15	0.70	0.13	0.02	0	-	0	0	1420
21	0.16	0.67	0.11	0.06	30	A	2	0.4	840
22	0.16	0.65	0.17	0.02	30	B	3	0.4	835
23	0.17	0.66	0.17	0	20	A	0	0.2	1150
24	0.15	0.70	0.13	0.02	10	A	15	0.4	840
25	0.16	0.65	0.18	0.01	7	A	3	6.0	860
26	0.17	0.67	0.10	0.06	10	B	3	0	960
27	0.17	0.66	0.17	0	20	G	-	-	900
28	0.15	0.70	0.13	0.02	19	H	-	-	900

TABLE 4

KIND OF GLASS	GLASS POWDER COMPOSITION (wt%)						SOFTENING POINT (°C)
A	PbO (84)	ZnO (7)	B_2O_3 (9)				315
B	PbO (80)	ZnO (10)	B_2O_3 (10)				310
C	PbO (52)	ZnO (4)	B_2O_3 (6)	GeO_2 (31)	Li_2O (7)		417
D	PbO (56)	ZnO (5)	B_2O_3 (6)	GeO2 (33)			480
E	PbO (51)	ZnO (4)	B_2O_3 (5)	GeO_2 (30)	Li_2O (6)	Sb_2O_3 (4)	442
F	PbO (74)	PbF_2 (10)	B_2O_3 (9)	ZnO (7)			275
G	B_2O_3 (35)	SiO_2 (45)	Al_2O_3 (10)	BaO (10)			650
H	B_2O_3 (24)	SiO_2 (35)	BaO (41)				690

TABLE 5

	ELECTRIC CHARACTERISTICS		
	ε_r	Q	τ_f ppm/°C
EXAMPLE			
23	75.0	1590	37
24	77.0	1260	21
25	72.0	1110	10
26	70.5	925	6
27	69.0	660	4
28	78.0	1105	37
29	72.0	790	32
30	71.0	620	23
31	74.0	1310	31
32	73.5	1250	17
33	72.0	1000	-3
34	63.0	720	-16
35	70.0	1090	32
36	66.0	1100	27
37	61.0	980	21
38	73.0	1180	33
39	75.0	1120	42
40	78.0	1090	47
41	74.0	820	54
42	66.0	1150	-19
43	69.0	780	-20
44	60.0	850	5
45	61.5	920	-12
46	61.0	1000	16
47	68.0	1250	-8
COMPARATIVE EXAMPLE			
13	47.0	160	14
14	NO RESONANCE		
15	68.0	310	166
16	41.0	210	76
17	45.0	100	36
18	65.0	320	110
19	44.0	280	-2
20	87.0	2870	18
21	31.0	210	19
22	26.0	160	31
23	96.0	100	85
24	43.0	250	-19
25	NO RESONANCE		
26	70.0	750	-7
27	NO SINTERING		
28	NO SINTERING		

Example 48

Barium carbonate powder ($BaCO_3$; 0.15 mole), titanium oxide powder (TiO_2; 0.675 mole), neodymium oxide powder (Nd_2O_3; 0.13 mole), samarium oxide powder (Sm_2O_3; 0.02 mole) and bismuth oxide powder (Bi_2O_3; 0.025 mole) were charged in a ball mill together with ethanol and then subjected to wet blending for 12 hours. After the removal of the solvent from the dispersion, the mixture was pulverized and then calcined at 1100°C in the air. Separately, glass powder A comprising 84wt% of lead oxide powder (PbO), 7 wt% of zinc oxide powder (ZnO) and 9 wt% of boron oxide powder (B_2O_3) was prepared according to the usual method. To the calcined product prepared above, there were added 2 wt% of the glass powder A comprising PbO, ZnO and B_2O_3, and 2 wt% of germanium oxide powder (GeO_2), followed by introducing the mixture into a ball mill together with ethanol and then wet blending for 12 hours. After the removal of the solvent from the dispersion, the mixture was pulverized, followed by addition of an appropriate amount of a polyvinyl alcohol solution to the pulverized product, drying the mixture, forming it into pellets having a diameter of 12 mm and a thickness of 4 mm and then firing the pellets at 1150 °C for 2 hours in the air. The composition of the product and the sintering temperature thereof are summarized in the following Table 6.

The ceramic composition thus prepared was inspected for various characteristic properties which were determined under the same conditions used in Example 23. The results thus obtained are listed in the following Table 6.

The ceramic composition thus prepared was processed into pieces each having a diameter of 7 mm and a thickness of about 3 mm and inspected for the specific dielectric constant ε_r, the unloaded Q and the temperature coefficient τ_f of the resonance frequency at a resonance frequency (ranging from 3 to 5 GHz) according to the dielectric resonance method. The results thus obtained are listed in the following Table 7.

Examples 49 to 61 and Comparative Examples 29 to 47

The same procedures used in Example 48 were repeated except that the mixing ratio of barium carbonate, titanium oxide, neodymium oxide, samarium oxide and bismuth oxide; the kinds and the added amount of glass powder comprising PbO, ZnO and B_2O_3 (glass powder B: 80 wt% PbO, 10 wt% ZnO and 10 wt% B_2O_3) and the added amounts of the minor component GeO_2 as well as the added amount (d) of the third component were changed as detailed in Table 6 to prepare dielectric ceramic compositions and they were inspected for characteristic properties in the same manner

used in Example 48. The results thus obtained are summarized in Table 7.

TABLE 6

	COMPOSITION OF DIELECTRIC CERAMIC									CALCINATION TEMPERATURE °C
	BaO x	TiO_2 y	Nd_2O_3 z	Sm_2O_3 t	Bi_2O_3 w	GLASS POWDER wt%	KIND OF GLASS	GeO_2 wt%	d wt%	
EXAMPLE										
48	0.15	0.675	0.13	0.02	0.025	2	A	2	-	1050
49	0.12	0.675	0.13	0.05	0.025	7	A	2	-	950
50	0.17	0.695	0.10	0.01	0.025	10	A	2	-	930
51	0.15	0.675	0.13	0.02	0.025	15	A	2	-	920
52	0.15	0.675	0.13	0.02	0.025	20	A	2	-	910
53	0.15	0.675	0.13	0.02	0.025	10	A	3	-	930
54	0.15	0.675	0.13	0.02	0.025	10	A	2	1(Nb_2O_5)	910
55	0.15	0.675	0.13	0.02	0.025	10	A	2	1(MnO)	920
56	0.15	0.675	0.13	0.02	0.025	10	A	2	1(Al_2O_3)	930
57	0.15	0.675	0.13	0.02	0.025	10	A	2	1(ZnO)	930
58	0.15	0.675	0.13	0.02	0.025	3	B	3	-	1050
59	0.12	0.675	0.13	0.05	0.025	8	B	2	-	950
60	0.17	0.695	0.10	0.01	0.025	11	B	2	-	940
61	0.15	0.675	0.13	0.02	0.025	15	B	5	-	920
COMPARATIVE EXAMPLE										
29	0.05	0.75	0.18	0.01	0.01	10	A	5	-	960
30	0.30	0.57	0.10	0.02	0.01	8	A	2	-	920
31	0.08	0.85	0.05	0.01	0.01	15	A	3	-	900
32	0.15	0.45	0.37	0.01	0.02	9	A	2	-	920
33	0.11	0.57	0.30	0.01	0.01	10	A	2	-	930
34	0.15	0.81	0	0.01	0.03	10	A	2	-	920
35	0.15	0.675	0.15	0	0.025	8	A	2	-	910
36	0.12	0.545	0.01	0.30	0.025	5	A	2	-	990
37	0.15	0.675	0.155	0.02	0	8	A	3	-	1030
38	0.15	0.60	0.13	0.02	0.10	5	A	2	-	990
39	0.15	0.675	0.13	0.02	0.025	0	-	0	-	1350
40	0.15	0.675	0.13	0.02	0.025	30	A	2	-	870
41	0.15	0.675	0.13	0.02	0.025	30	B	2	-	890
42	0.15	0.675	0.13	0.02	0.025	8	A	0.1	-	1250
43	0.15	0.675	0.13	0.02	0.025	8	A	15	-	850
44	0.15	0.675	0.13	0.02	0.025	10	A	2	5(Nb_2O_5)	940
45	0.15	0.675	0.13	0.02	0.025	10	A	2	5(MnO)	900
46	0.15	0.675	0.13	0.02	0.025	10	A	2	5(Al_2O_3)	900
47	0.15	0.675	0.13	0.02	0.025	10	A	2	5(ZnO)	900

TABLE 7

	ELECTRIC CHARACTERISTICS		
	ε_r	Q	τ_f ppm/°C
EXAMPLE			
48	81.0	1150	7
49	74.0	930	-22
50	77.0	800	-12
51	77.0	1100	-13
52	78.0	950	-30
53	77.0	450	-14
54	76.0	820	-3
55	77.0	560	4
56	74.0	620	2
57	78.0	750	-8
58	80.0	1050	7
59	73.0	890	-21
60	74.0	720	-11
61	73.0	630	-17
COMPARATIVE EXAMPLE			
29	51.0	120	-12
30	NO RESONANCE		
31	70.0	400	130
32	41.0	170	33
33	49.0	80	-15
34	43.0	130	-35
35	80.0	130	-26
36	46.0	240	-38
37	79.0	1050	33
38	41.0	200	33
39	93.0	1200	5
40	33.0	180	-7
41	29.0	150	-5
42	85.0	1100	-33
43	45.0	200	-55
44	74.0	210	25
45	77.0	250	33
46	72.0	220	27
47	71.0	240	22

Example 62

Barium carbonate powder ($BaCO_3$; 0.13 mole), titanium oxide powder (TiO_2; 0.69 mole), neodymium oxide powder (Nd_2O_3; 0.16 mole) and bismuth oxide powder (Bi_2O_3; 0.02 mole) were charged in a ball mill together with ethanol and

then subjected to wet blending for 12 hours. After the removal of the solvent from the dispersion, the mixture was pulverized and then calcined at 1250°C in the air. Separately, glass powder A comprising 84wt% of lead oxide powder (PbO), 7 wt% of zinc oxide powder (ZnO) and 9 wt% of boron oxide powder (B_2O_3) was prepared according to the usual method. To the calcined product prepared above, there were added 2 wt% of the glass powder A comprising PbO, ZnO and B_2O_3, 3 wt% of germanium oxide powder (GeO_2) and 1 wt% (corresponding to 0.4 wt% as expressed in terms of the weight of Li_2O) of lithium carbonate powder (Li_2CO_3), followed by introduction of the mixture into a ball mill together with ethanol and then wet blending for 48 hours. After the removal of the solvent from the dispersion, the mixture was pulverized, followed by addition of an appropriate amount of a polyvinyl alcohol solution to the pulverized product, drying the mixture, forming it into pellets having a diameter of 12 mm and a thickness of 4 mm and then firing the pellets at 945°C for 2 hours in the air. The composition of the product and the sintering temperature thereof are summarized in the following Table 8.

The ceramic composition thus prepared was processed into pieces each having a diameter of 7 mm and a thickness of about 3 mm and inspected for the specific dielectric constant ε_r, the unloaded Q and the temperature coefficient τ_f of the resonance frequency at a resonance frequency (ranging from 3 to 6 GHz) according to the dielectric resonance method. The results thus obtained are listed in the following Table 9.

Examples 63 to 82 and Comparative Examples 48 to 62

The same procedures used in Example 62 were repeated except that the mixing ratio of barium carbonate, titanium oxide, neodymium oxide, samarium oxide and bismuth oxide; the kinds of glass powder comprising PbO, ZnO and B_2O_3 (glass powder B: 80 wt% PbO, 10 wt% ZnO and 10 wt% B_2O_3) and the added amounts of the minor components were changed as detailed in Table 8 to prepare dielectric ceramic compositions and they were inspected for characteristic

properties. The results thus obtained are summarized in Table 9.

TABLE 8

	COMPOSITION OF DIELECTRIC CERAMIC									CALCINATION TEMPERATURE °C
	BaO x	TiO_2 y	Nd_2O_3 z	Sm_2O_3 t	Bi_2O_3 w	GLASS POWDER wt%	KIND OF GLASS	GeO_2 wt%	Li_2O wt%	
EXAMPLE										
62	0.13	0.69	0.16	0	0.02	2	A	3	0.4	945
63	0.17	0.66	0.11	0.04	0.02	7	A	3	0.2	920
64	0.17	0.66	0.10	0.04	0.03	10	A	3	0.2	890
65	0.18	0.66	0.11	0.04	0.01	15	A	3	0.2	880
66	0.15	0.67	0.10	0.06	0.02	20	A	2	0.4	860
67	0.17	0.66	0.12	0.03	0.02	5	B	5	0.4	960
68	0.17	0.66	0.10	0.06	0.01	10	B	3	0.8	920
69	0.16	0.64	0.16	0.02	0.02	15	B	3	0.4	900
70	0.13	0.69	0.16	0	0.02	7	A	3	0.4	920
71	0.12	0.70	0.14	0.02	0.02	7	A	3	0.4	920
72	0.13	0.69	0.11	0.05	0.02	7	A	3	0.4	920
73	0.14	0.70	0.04	0.10	0.02	10	A	5	0.2	920
74	0.17	0.66	0.16	0	0.01	10	A	5	0.2	900
75	0.16	0.66	0.16	0	0.02	10	A	7	0.2	915
76	0.16	0.66	0.16	0	0.02	10	A	10	0.2	920
77	0.15	0.65	0.17	0.01	0.02	7	A	3	0.2	925
78	0.15	0.65	0.17	0.01	0.02	7	A	3	0.4	905
79	0.15	0.65	0.17	0.01	0.02	7	A	3	0.6	900
80	0.15	0.65	0.17	0.01	0.02	7	A	3	0.8	875
81	0.14	0.67	0.17	0	0.02	10	A	5	0.4	860
82	0.14	0.67	0.17	0	0.02	15	A	3	0.4	845
COMPARATIVE EXAMPLE										
48	0.05	0.75	0.18	0.01	0.01	10	A	5	0.2	935
49	0.30	0.57	0.10	0.02	0.01	10	A	3	0.2	920
50	0.08	0.86	0.04	0.01	0.01	15	A	3	0.4	880
51	0.14	0.45	0.38	0.01	0.02	9	A	2	0.6	890
52	0.11	0.56	0.31	0.01	0.01	10	A	2	0.8	885
53	0.10	0.87	0	0.01	0.02	10	A	2	0.4	905
54	0.13	0.55	0.01	0.30	0.01	5	A	3	0.4	915
55	0.18	0.67	0.14	0.01	0	2	A	2	1.5	955
56	0.20	0.64	0.05	0.01	0.1	7	A	3	0.4	910
57	0.14	0.69	0.13	0.02	0.02	0	-	0	0	1400
58	0.15	0.67	0.11	0.06	0.01	30	A	2	0.4	850
59	0.15	0.65	0.16	0.02	0.02	30	B	3	0.4	820
60	0.16	0.66	0.16	0	0.02	20	A	0	0.2	1130
61	0.14	0.70	0.13	0.02	0.01	10	A	15	0.4	835
62	0.16	0.65	0.17	0.01	0.01	7	A	3	6.0	855
63	0.16	0.67	0.10	0.06	0.01	10	B	3	0	950

TABLE 9

	ELECTRIC CHARACTERISTICS		
	ε_r	Q	τ_f ppm/°C
EXAMPLE			
62	76.0	1450	35
63	78.0	1160	18
64	73.0	1110	5
65	71.0	900	4
66	70.0	640	2
67	79.0	1050	35
68	73.0	760	29
69	81.0	1200	73
70	75.0	1250	29
71	74.0	1050	15
72	73.0	990	-5
73	64.0	730	-18
74	71.0	1100	30
75	67.0	1050	25
76	62.0	950	19
77	74.0	1080	30
78	76.0	1020	40
79	79.0	1050	43
80	75.0	800	50
81	68.0	1100	-22
82	70.0	790	-22
COMPARATIVE EXAMPLE			
48	49.0	170	13
49	NO RESONANCE		
50	69.0	300	150
51	43.0	190	72
52	47.0	90	30
53	66.0	350	105
54	47.0	310	-5
55	60.0	390	47
56	47.0	180	-15
57	88.0	2770	15
58	35.0	240	23
59	29.0	170	29
60	97.0	120	75
61	45.0	230	-22
62	NO RESONANCE		
63	71.0	650	-10

As has been discussed above in detail, the dielectric ceramic composition of the present invention exhibits excellent characteristic properties in that it has a large specific dielectric constant ε_r, a large unloaded Q and a small temperature

coefficient of the resonance frequency and the composition is advantageous in that it can be sintered at a low temperature and that it can easily be laminated together with, for instance, an Ag, Ag-Pd or Cu internal electrode.

Claims

1. A dielectric ceramic composition mainly comprising a major component which comprises barium, titanium, neodymium, samarium and oxygen and is represented by the following compositional formula:

$$xBaO\text{-}yTiO_2\text{-}zNd_2O_3\text{-}tSm_2O_3 \quad (1)$$

(wherein $0.1 \leqq x \leqq 0.2$; $0.5 \leqq y \leqq 0.8$; $0.01 \leqq z \leqq 0.2$; $0 \leqq t \leqq 0.2$, provided that $x+y+z+t = 1$); and
a minor component mainly comprising glass powder, which mainly comprises PbO, ZnO and B_2O_3, and GeO_2, and wherein
the content (a) (% by weight) of the glass powder falls within the range of $1 \leqq a \leqq 25$ and the content (b) (% by weight) of GeO_2 falls within the range of $0.5 \leqq b \leqq 10$, on the basis of the weight of the major component.

2. The dielectric ceramic composition of claim 1 which further comprises Li_2O as a minor component and the content (c) (% by weight) of Li_2O falls within the range of $0.04 \leqq c \leqq 4$ on the basis of the weight of the major component.

3. The dielectric ceramic composition of claim 1 or 2 which further comprises at least one member selected from the group consisting of Nb_2O_5, MnO, Al_2O_3 and ZnO.

4. The dielectric ceramic composition of claim 1, 2 or 3 wherein the content of PbO, ZnO and B_2O_3 are $5 \leqq PbO \leqq 90$, $5 \leqq B_2O_3 \leqq 60$ and $0 < ZnO \leqq 65$ (% by weight).

5. The dielectric ceramic composition of claim 4 wherein the softening point of the glass powder is about 100 °C to about 500°C.

6. A dielectric ceramic composition mainly comprising a major component which comprises barium, titanium, neodymium, samarium, bismuth and oxygen and is represented by the following compositional formula:

$$xBaO\text{-}yTiO_2\text{-}zNd_2O_3\text{-}tSm_2O_3\text{-}wBi_2O_3 \quad (2)$$

(wherein $0.1 \leqq x \leqq 0.2$; $0.5 \leqq y \leqq 0.8$; $0.01 \leqq z \leqq 0.2$; $0.01 \leqq t \leqq 0.2$; $0.005 \leqq w \leqq 0.05$, provided that $x+y+z+t+w = 1$); and
a minor component mainly comprising glass powder, which mainly comprises PbO, ZnO and B_2O_3, and GeO_2, and wherein
the content (a) (% by weight) of the glass powder falls within the range of $1 \leqq a \leqq 25$ and the content (b) (% by weight) of GeO_2 falls within the range of $0.5 \leqq b \leqq 10$, on the basis of the weight of the major component.

7. The dielectric ceramic composition of claim 6 which further comprises Li_2O as another minor component and the content (c) (% by weight) of Li_2O falls within the range of $0.04 \leqq c \leqq 4$ on the basis of the weight of the major component.

8. The dielectric ceramic composition of claim 6 or 7 which further comprises at least one member selected from the group consisting of Nb_2O_5, MnO, Al_2O_3 and ZnO.

9. The dielectric ceramic composition of claim 6, 7 or 8 wherein the content of PbO, ZnO and B_2O_3 are $5 \leqq PbO \leqq 90$, $5 \leqq B_2O_3 \leqq 60$, and $0 < ZnO \leqq 65$ (% by weight).

10. The dielectric ceramic composition of claim 9 wherein the softening point of the glass powder is about 100 °C to about 500°C.

11. A dielectric device such as a dielectric resonator and a dielectric filter, comprising a dielectric ceramic composition according to any one of claims 1 to 10.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 3625

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DATABASE WPI Week 8215 Derwent Publications Ltd., London, GB; AN 82-29982E & JP-A-57 040 806 (TDK) , 6 March 1982 * abstract *	1,11	C04B35/468 H01B3/12 H01G4/12
A	DATABASE WPI Week 9207 Derwent Publications Ltd., London, GB; AN 92-52757 & JP-A-03 295 854 (SUMITOMO METAL) , 26 December 1991 * abstract *	1,4,6,9, 11	
Y	EP-A-0 551 100 (E.I.DU PONT DE NEMOURS) * page 3, line 24 - page 4, line 37; claims *	6,8	
A	* the whole document *	1,4,5, 9-11	
Y	EP-A-0 473 347 (NGK INSULATORS) * abstract; claims *	6,8	
A	* the whole document *	1,3,11	
A	DATABASE WPI Week 9404 Derwent Publications Ltd., London, GB; AN 94-29075 & JP-A-05 334 914 (SUMIZOMO METAL) * abstract *	1,4-6, 9-11	

-/--

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C04B
H01B
H01G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 December 1995	Harbron, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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EUROPEAN SEARCH REPORT

Application Number
EP 95 11 3625

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DATABASE WPI Week 9416 Derwent Publications Ltd., London, GB; AN 94-129441 & JP-A-06 076 627 (TAIYO YUDEN) , 18 March 1994 * abstract * ---	1,2,6,7	
A	GB-A-2 068 931 (CENTRALAB INC.) ---		
A	EP-A-0 412 440 (OKI ELECTRIC INDUSTRY) ---		
A	DATABASE WPI Week 8943 Derwent Publications Ltd., London, GB; AN 89-314692 & JP-A-01 234 358 (MATSUSHITA) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 December 1995	Harbron, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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EPO FORM 1503 03.82 (P04C01)